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Effect of the content of MnO on the electric-dielectric properties of potassium-phosphate glasses

W. Ahmina[1], M. El Moudane[2], M. Zriouil[1], M. Taibi[3]

[1] *Laboratoire de Chimie du Solide Appliquée, Université Mohammed V de Rabat, Faculté des Sciences, Av. Ibn Battouta, B.P. 1014, Rabat, Morocco.*

[2] *Laboratoire des Matériaux, Nanotechnologies et Environnement, Université Mohammed V de Rabat, Faculté des Sciences, Av. Ibn Battouta, B.P. 1014, Rabat, Morocco.*

[3] *Laboratoire de Physico-Chimie des Matériaux associé à l'AUF (LAF 502), Université Mohammed V de Rabat, Ecole Normale, Supérieure Takadoum, B.P. 5118 Rabat, Morocco.*

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m.elmoudane@gmail.com
Phone: (+212) 662379885

Abstract

This paper deals with the investigation of the electrical conductivity and dielectric properties, including dielectric constant (ε'), dielectric losses (tanδ) and ionic conductivity (σ) as a function of temperature ranging from room temperature to 540 °C at a fixed applied frequency of 100 kHz for some phosphate glasses in the ternary K_2O-MnO-P_2O_5 system. The compositions chosen for the study are (50-x)K_2O-xMnO-50P_2O_5 (20-35 mol%) and xK_2O-20MnO-(80-x)P_2O_5 (15-30 mol%), which were prepared by the conventional melt quenching technique. The amorphous nature of the samples was asserted by X–ray diffraction. The values of the dielectric parameters (viz., ε', tan δ and σ) decrease by increasing manganese oxide concentration and increase by increasing temperature. The observed decrease in the dielectric parameters, with increasing amount of MnO, can be explained as the result of formation of more compact and integrated glass structure, leading to a decrease of the polarization. The conductivity-temperature data obeys to the classical Arrhenius relationship. The ionic conductivity σ increases substantially with increasing concentration of potassium oxide and diminishes with increasing concentration of MnO. The activation energy values of the studied glasses were calculated the structural role of manganese oxide was determinate.

1. Introduction

Glasses based on P_2O_5 are both scientifically and technologically important materials, because they offer some physical properties better than silicate and borate glasses, due to their superior physical properties, such as high thermal expansion coefficient, low melting and softening temperatures and high ultra-violet and far infrared transmissions [1]. It was found important applications in e.g. glass-to-metal seals, laser hosts and biocompatible materials.

The phosphate network is based on corner-sharing PO_4 units which form chains and rings or isolated PO_4 groups [2]. When modifier cations are added to phosphate glasses, the P=O of phosphate groups is unaffected, and depolymerization takes place through the breaking linkages only. On the other hand, the introduction of transitional metal ions, such as MnO in glasses, leads to a change in glass structure, electrical, optical and magnetic properties [3-5].

In addition, the MnO-containing phosphate glasses, incorporating of monovalent alkali metal cations (Li^+, Na^+, K^+), are interesting in connection with the ionic conductivity [6-9]. Dielectric properties of glasses are importantly taken into account in the construction of receiving equipment, where a much lower energy level is involved. Study of electrical and dielectric properties, especially, the dielectric permittivity, dissipation factor and electrical conductivity of the glasses, helps in assessing their insulating character and also throw light on structural aspects of the glasses. In the last decade, many works along these lines were carried out on a variety of glassy materials by a number of researchers yielding valuable information [10-12]. Recently, thermal and structural properties of K_2O-MnO-50P_2O_5 glasses have been studied by means of differential scanning calorimetry (DSC), Fourier-Transform Infrared (FTIR) measurements and Raman spectroscopy, and the partial glass-forming ability of Mn^{2+} is discussed [13-14].

The main objective of the present work is to make a comprehensive analysis on the role of manganese ions on the dielectric aspects of potassium phosphates glasses from a systematic study on dielectric properties. Two series of phosphate glasses of the general formulae (50-*x*)K_2O-*x*MnO-50P_2O_5, *x* = 20, 25, 30, and 35 mol% and

$x$$K_2O$-20MnO-(80-$x$)$P_2O_5$, x = 15, 20, 25, and 30 mol% were prepared. Their electrical and dielectric properties such as, ionic conductivity (σ), dielectric constant ε', and dielectric losses (tanδ) were determined and the effects of manganese and temperature on the electric-dielectric properties are discussed.

2. Experimental

Glasses were prepared using analytical-grade K_2CO_3, $MnCO_3$ and $NH_4H_2PO_4$. Batches of 4 or 6 g were weighed to prepare glass compositions of (50-x)K_2O-xMnO-50P_2O_5 (20-35 mol%) and xK_2O-20MnO-(80-x)P_2O_5 (15-30 mol%). The batches were introduced in an alumina crucible and melted at 1100°C during 30 min. Details of the procedure, adopted in the preparation of these glasses, have been described in our earlier work [13].

The amorphous state of all as-quenched samples was confirmed by powder X-ray diffractometry (XRD), using a Phillips D5000 apparatus equipped with a CuKα X-ray source and a Ni filter (λ = 1.54 Å). No Bragg peaks were detected in a wide range of 2θ angles between 10°and 80°.

Electrical measurements were carried out on samples shaped as disks with two parallel faces. The disks were fired at 100°C for 1 h, and the surfaces were painted with silver paste. Each disk was placed between silver electrodes; slight pressure was applied to make good electrical contact. The dielectric constant (ε') and ionic conductivity (σ) were deduced from the measurements of capacitance C and dissipation factor tanδ at 100 kHz in the room temperature to 540 °C using an automatic controlled LCR meter type HP 4284A.The dielectric constant (ε') and ionic conductivity (σ) were expressed as the following:

$$\boldsymbol{\varepsilon' = \frac{Cd}{\varepsilon_0 A}} \quad (1)$$

$$\sigma = \omega \varepsilon_0 \varepsilon' \tan\delta \quad (2)$$

Where $\boldsymbol{\varepsilon_0}$ is the permittivity of free space, ω is the applied frequency multiplied by 2π, d is thickness of the glass sample and A is cross sectional area of the sample.

All the measurements were undertaken along the two lines denoted A and B (Fig.1), which correspond to (50-x)K_2O-xMnO-50P_2O_5 and $x$$K_2O$-20MnO-(80-$x$)$P_2O_5$ glasses, respectively.

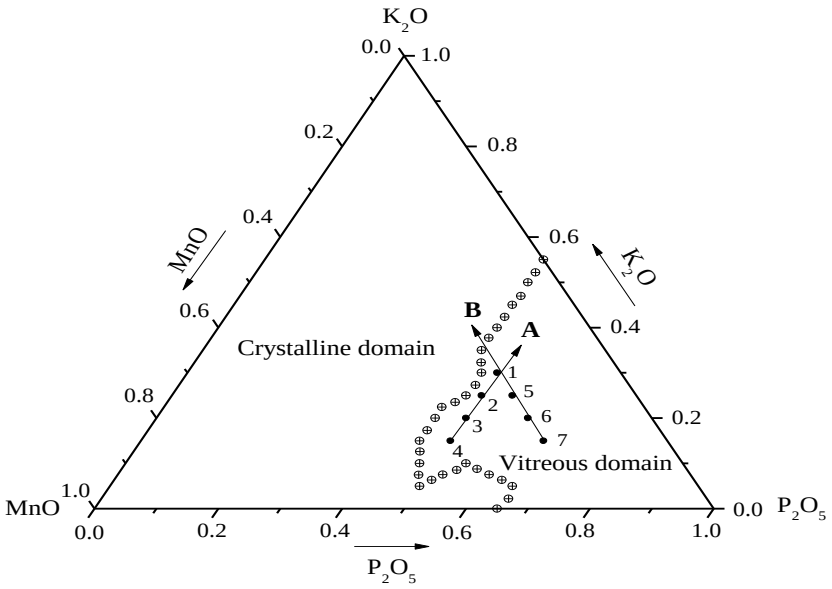

Figure 1: The glass-forming region in the ternary system K_2O-MnO-P_2O_5 at 1100 °C [13]

3. Results

3.1. *Dielectric constant* (ε') *and dielectric loss behaviour* $(tan\delta)$

The dielectric constant (ε′), at different temperatures, of all the studied glassy materials, containing different concentrations of K_2O and MnO, measured at 100 kHz, are shown in figures 2 and 3. Dielectric constant ε′ is increasing with temperature slowly up to about 180 °C. Beyond this temperature, it's observed to increase at faster rate. The increase rate of ε' with temperature is found to be the largest for glasses containing the highest concentration of K_2O and observed to be the lowest for the glasses containing the lowest concentration of MnO. The same trend was observed in many other phosphates glasses [15-16].

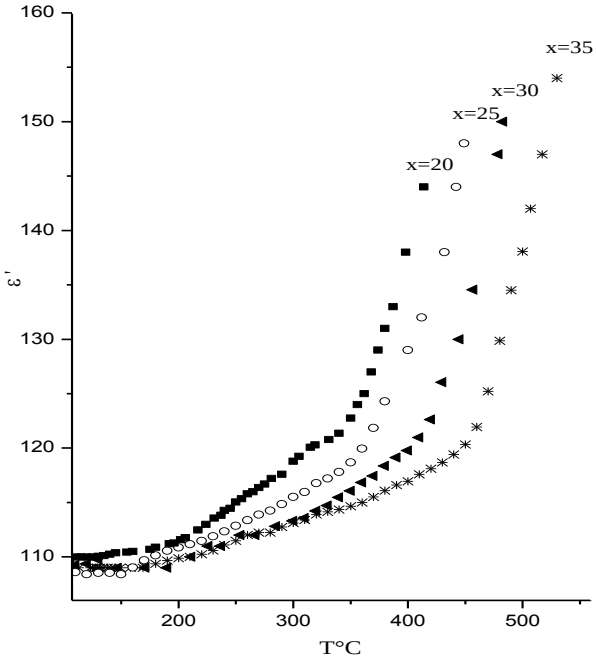

Figure 2: A comparison plot of variation of dielectric constant ε' with temperature for (50-*x*)K_2O- *x*MnO-50P_2O_5 glasses at 100 kHz.

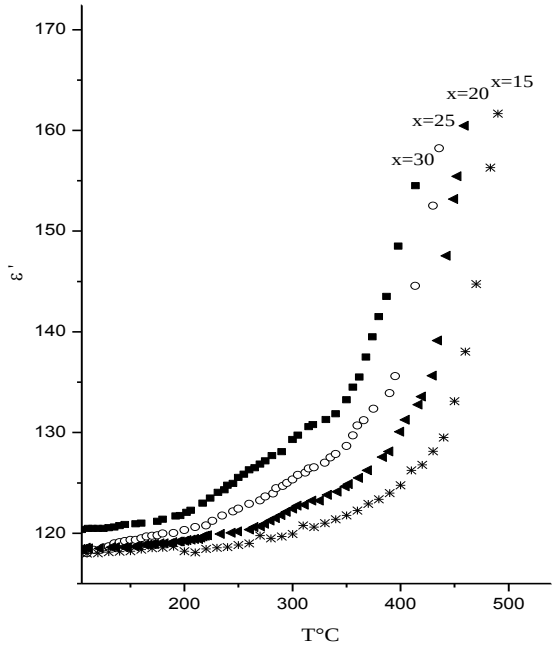

Figure 3: A comparison plot of variation of dielectric constant ε' with temperature for *x*K_2O-20MnO-(80-*x*)P_2O_5 glasses at 100 kHz.

The factor, which means the phase difference, due to the loss of energy, within the sample at a particular frequency, is the loss factor tangent, tanδ. The temperature dependence at 100 kHz for all the studied glass along the lines A and B is shown in Figures 4 and 5, respectively. It can be noted that, the values of dielectric losses show little variation with composition up to about 250 °C for all studied glassy materials. Beyond this temperature, dielectric loss shows a stronger dependence of temperature and compositions. Indeed, when K_2O is progressively substituted by MnO, through maintaining the amount of P_2O_5 constant at 50 mol%, we need to heat more and more to increase the dielectric loss. This confirms the fact that manganese ions can increase the electrical stability of phosphate glasses [17]. When the molar percentage of MnO is kept constant at 20 mol% and P_2O_5 is replaced by MnO in *x*K_2O-20MnO-(80-*x*)P_2O_5 (x = 15-30 mol%), the values of dielectric losses increase largely with K_2O concentration.

3.2. Ionic conductivity

Figures 6 and 7 show the variation of the ionic conductivity, with the reciprocal temperature, for all the studied compositions in the temperature range 150-480 °C, since no significant variation has been observed below 150°C. It can be seen from these figures that as temperature increases, the conductivity increases. This indicates that the plots obey Arrhenius rule:

$$\sigma = \sigma_0 exp\left(\frac{E_a}{K_B T}\right) \quad (3)$$

Where E_a is the activation energy, σ_0 is the pre-exponential factor, K_B is the Boltzmann constant and T is the absolute temperature (K). It is observed that the conductivity is strongly dependent on K_2O and MnO amounts. It is clear from the figures 6 and 7, and table 1 that the conductivity decreases with increasing of MnO content. Therefore, it is understood that the conductivity in these glasses is mainly due to the potassium ions.

The values of activation energy for conduction, extracted from the straight line slope of logσ, against reciprocal temperature 1000/T, are listed in Table 1 and plotted in Figure 8. From Table 1 and Figure 8, it may be noted that the values of activation energy of conduction, for different glass samples, are reduced with increasing amount of K_2O and increase with rising concentration of MnO. Thus, the increase in Ea and the decrease in σ may be consistent with the partially-forming character of the manganese oxide. Similar results have been observed in many other oxide glasses.

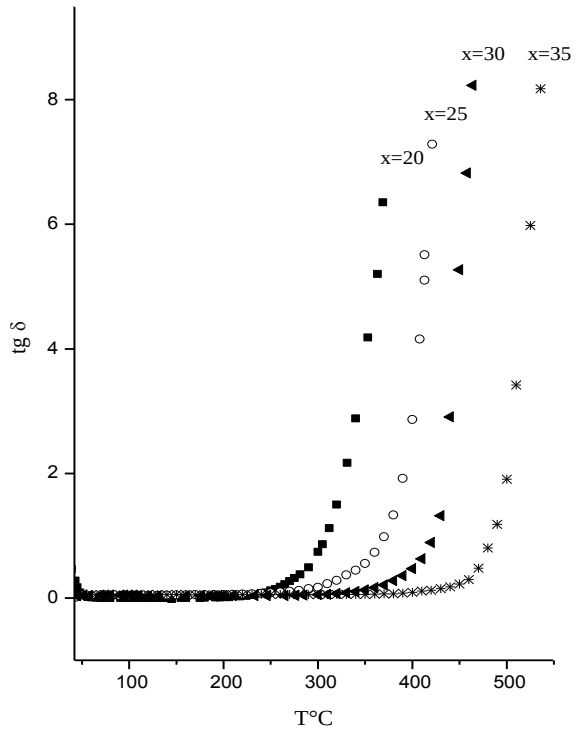

Figure 4: Variation of loss factor tanδ with temperature for different concentrations of MnO in (50-*x*)K_2O-*x*MnO-50P_2O_5 glasses at 100 kHz.

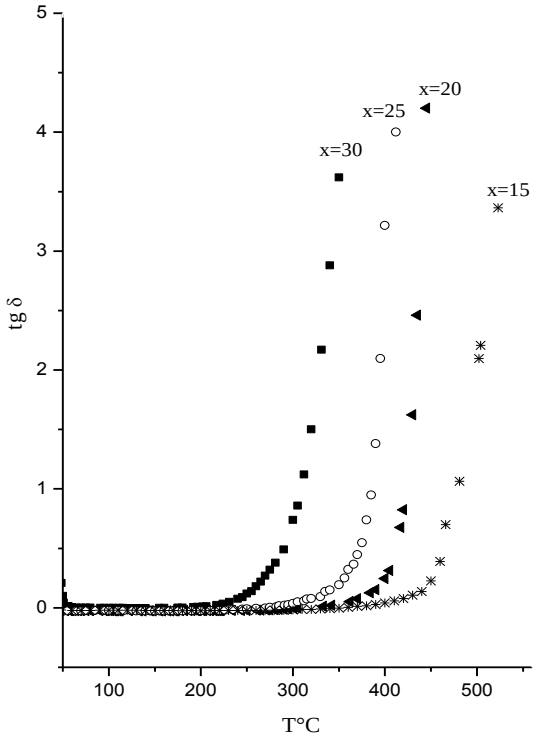

Figure 5: Variation of loss factor tanδ with temperature for different concentrations of K_2O in *x*K_2O-20MnO-(80-*x*)P_2O_5 glasses at 100 kHz.

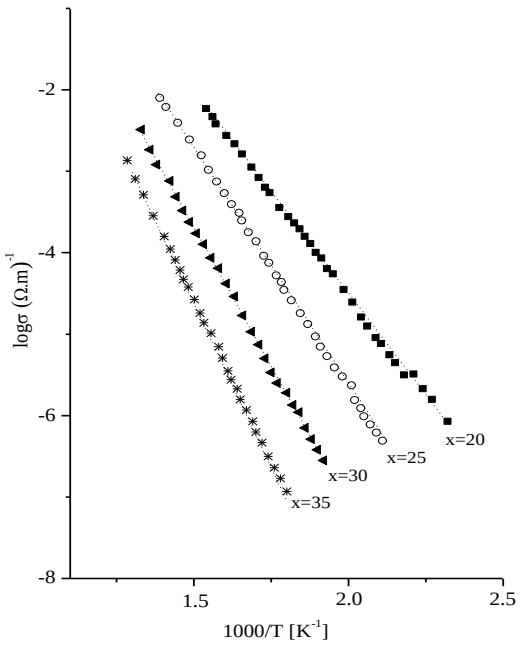

Figure 6: Variation of σ with 10^3/T for (50-*x*)K_2O-*x*MnO-50P_2O_5 glasses at 100 kHz.

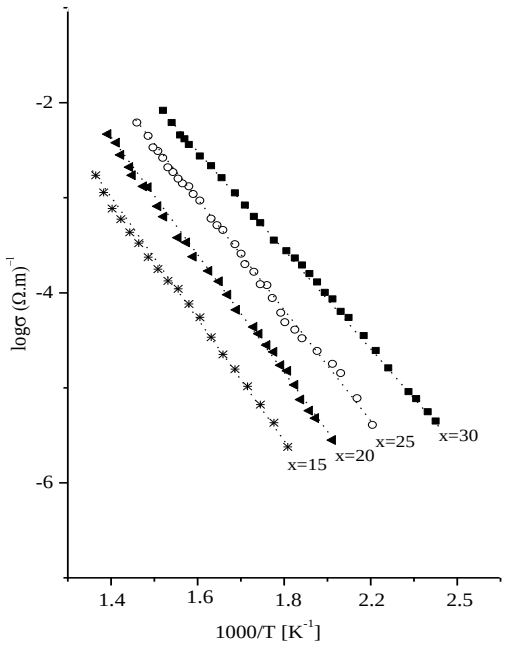

Figure 7: Variation σ with 10^3/T for *x*K_2O-20MnO-(80-*x*)P_2O_5 glasses at 100 kHz.

Table 1: Glass compositions (mol %), ionic conductivity σ ($\Omega^{-1}.cm^{-1}$), and activation energy E_a (eV) at a selected temperatures of the studied glasses.

Glass no.	K_2O	MnO	P_2O_5				E_a
1	30	20	50	$2.75x10^{-4}$	$5.88x10^{-4}$	$1.12x10^{-3}$	1.01
2	25	25	50	$3.16x10^{-5}$	$7.58x10^{-5}$	$1.69x10^{-4}$	1.17
3	20	30	50	$1.77x10^{-6}$	$4.26x10^{-6}$	$1.14x10^{-5}$	1.38
4	15	35	50	10^{-7}	$2.81x10^{-7}$	$9.12x10^{-7}$	1.58
5	25	20	55	$1.90x10^{-5}$	$4.07x10^{-5}$	$8.70x10^{-5}$	1.12
6	20	20	60	$6.16x10^{-6}$	$1.31x10^{-5}$	$2.57x10^{-5}$	1.24
7	15	20	65	$1.41x10^{-6}$	$3.31x10^{-6}$	$6.91x10^{-6}$	1.38

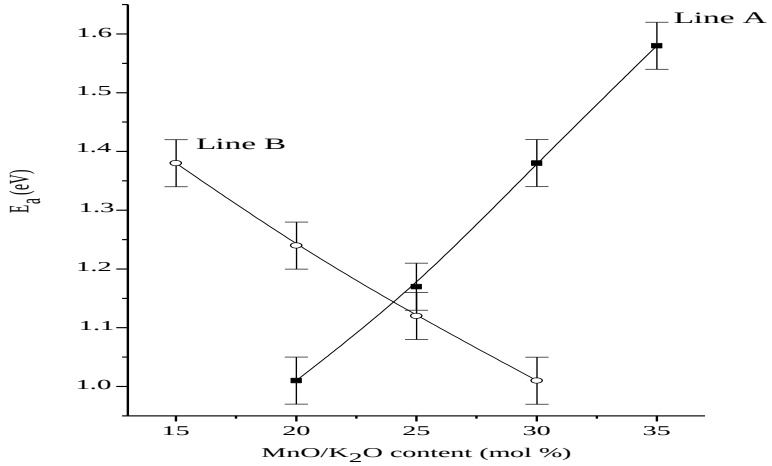

Figure 8: Variation of activation energy with MnO and K_2O contents in the studied glasses

4. Discussion

The study of the dielectric properties is an important source of valuable information about conduction process, since it can be used to understand the origin of dielectric losses, electrical and dipolar relaxation time and its activation energy [18]. The values of dielectric constant and loss tangent of all studied glasses show a strong dependence on the composition of K^+ and Mn^{2+} cations.

When K_2O is added in these glasses, the network of P_2O_5 is modified by the formation of the –P–O^-... K^+ entities, which create a large number of charge carriers K^+, that can easily move through the glass during heating. This fact contributes to an increase in the values of dielectric constant and loss tangent.

On the other hand, when MnO replaces K_2O, –P–$O^{\delta-}$...$Mn^{\delta+}$ bonds are formed with a stronger covalent character Mn–O bonds than the K–O bonds, which increases the cross-linking and the reticulation of the network. This means that the glasses will show low dielectric parameters. The formation of Mn-O bonds has been studied and discussed by FT-IR and Raman spectroscopy in our previous works [13-14].

The increase of dielectric constant of the glassy samples, with temperature, can be attributed to the fact that the dipoles in polar materials cannot orient themselves at low temperature. When the temperature is increased, the orientation of dipoles is facilitated and thus increases the value of the polarization's orientation, which increases ε' [19]. The temperature dependence of dielectric loss is very much similar to that of dielectric constant. Indeed, the origins of dielectric losses are the conduction losses, dipole losses and vibrational losses [20, 21]. As the temperature increases, the electrical conduction losses increase, which increases the value of tanδ [22].

The increase in conductivityσ, when P_2O_5 is substituted by K_2O in $x$$K_2O$-20MnO-(80-$x$)$P_2O_5$) glasses, can be explained by an increase in the number of carries K^+ and their mobility in the glass network. Indeed, when a modifier cation K^+ was incorporated into the glass matrix, it will short the phosphate chains by formation of non-bridging oxygen's, contributing to the formation of relatively open glass structure and offering the hopped sites for K^+ ions, which facilitate the movements of the charge carriers (K^+ ions) and enhance its jumps through glass network.

In the opposite variation, the substitution of potassium for manganese in $(50\text{-}x)K_2O\text{-}x MnO\text{-}50P_2O_5$ glasses causes an increase of the network cross-link strength by the formation of P-O-Mn linkages. Thus, the glass is expected to possess a more close structure. This restructuring process gives rise to the decrease in conduction due to the blocking conduction pathway for K^+ ions. The increase of E_a and the decrease in mobility of K^+ could be consistent with the origin of the partial glass-forming ability of Mn^{2+}. This behavior confirms our results obtained previously, for densities, molar volume, glass transition temperature, FT-IR and Raman measurements, regarding the reticulation of the glass system and therefore its stability [13, 14]. The same results have been reported for many other oxide glasses [23-26].

Conclusions

The electrical and dielectric properties of two series of phosphate glasses having the general formulae $(K_2O)_{50-x}(MnO)_x(P_2O_5)_{50}$ (x = 20-35 mol%) and $(K_2O)_x(MnO)_{20}(P_2O_5)_{80-x}$ (x = 15-30 mol%) were studied. Results of studies on the physical properties such as, dielectric constant, loss tangent and ionic conductivity show that all electrical and dielectric parameters decrease with increasing MnO content and increase with increasing temperature at a fixed frequency. The decrease in conductivity and the increase in activation energy, when MnO is substituted by K_2O, are attributed to the decreasing number of carriers and their mobility. This result shows that manganese oxide plays an intermediate character and it tends to play more a role of glass former with increasing MnO content. The observed decrease in the dielectric parameters, with increasing amount of MnO, can be explained as the result of formation of more compact and integrated glass structure, leading to a decrease of the polarization. The usual behavior of dielectric constant and loss tangent increasing with temperature can be explained by the increasing of the orientation polarization and the electrical conduction losses values.

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